PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-231266

(43)Date of publication of application : 10.09.1996

(51)Int.Cl. C04B 35/10
H01L 21/205
H01L 21/3065

(21)Application number : 07-270363

(22)Date of filing : 18.10.1995

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(30)Priority

Priority number : 94 325672 Priority date : 18.10.1994 Priority country : US

(54) PLASMA FLUORINE RESISTANT POLYCRYSTALLINE ALUMINA CERAMIC MATERIAL AND METHOD OF MAKING IT

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain polycrystalline alumina ceramic materials having extremely strong resistance against fluorine plasma by forming and sintering a base material using alumina powder having an unimodal grain distribution and a small amount of a binder.

SOLUTION: Alumina powder with an unimodal grain distribution having a center in about 0.5 to 2.0 μm is prepared by crushing alumina with a ball mill and sieving it. 99.1 to 99.8 wt.% of the alumina powder and 0.5 to 0.2 wt.% of a binder comprising a mixture of silica, CaO and MgO are mixed to form a base material with its density of about 1.8 to 2.2 g/cm3 by applying a pressure of 5,000 to 14,000 psi. The base material is then sintered without pressure in air for 1 to 10 hours at 1,400 to 1,700°C to obtain polycrystalline allumina ceramic materials having an unimodal grain distribution with the center between around 15 to 30 μm.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

CLAIMS

[Claim(s)]
[Claim 1] The polycrystal alumina ceramic material of plasma fluorine resistance.
[Claim 2] The ceramic material according to claim 1 which has a particle-size (grain size) distribution in the single mode (unimodal).
[Claim 3] The ceramic material according to claim 2 into which the particle size distribution in the aforementioned single mode has a center in between (about 15 micrometers and about 30 micrometers) (centered).
[Claim 4] The polycrystal alumina ceramic material of the plasma fluorine resistance which has the particle size distribution in the single mode which has a center in between (about 15 micrometers and about 30 micrometers) by the weight, including an about 99.5 wts% - 99.8wt% alumina and an about 0.5 to 0.2 wt% binder.
[Claim 5] (i) The manufacture technique of the polycrystal alumina ceramic material of the plasma fluorine resistance which contains the step which forms a base (green body), and the step which sinters (ii) this base from the fine particles which have the particle size distribution in the single mode, including an about 99.5 wts% - 99.8wt% alumina and an about 0.5 to 0.2 wt% binder.
[Claim 6] The ceramic material manufactured by technique according to claim 5.
[Claim 7] The product containing a ceramic material according to claim 1 (article of manufacture).
[Claim 8] The product containing a ceramic material according to claim 4.
[Claim 9] The product according to claim 7 which is a component (component) for using it with vacuum process equipment (vacuum processing apparatus).
[Claim 10] The product according to claim 9 chosen out of a chuck, a nozzle, a susceptor, a heater plate, a clamp ring, a shield ring, a wafer boat, and the group that consists of a chamber wall.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the improved alumina ceramic material by the fluorine plasma which carries out an etching pair and has very strong resistance (highly resistant). this invention relates to products (article of manufacutre), such as a component of the semiconductor process equipment containing the technique of producing the this improved ceramic material further, and the improved this ceramic material, or parts (components).
[0002]
[Description of the Prior Art] Generally semiconductor process equipment needs the component of resistance to a cruel chemistry environment. For example, between the processes of chamber cleaning, and in a chemistry gaseous-phase deposition (CVD) reactor, a typically high-density fluorine plasma environment is generated. The plasma (librated) fluorine isolated from a fluorocarbon and other fluorine inclusion gas (CF4 : for example, O2 plasma) is used in order to remove the dielectric-film residue (residue) deposited into the chamber of CVD reactor. A fluorine plasma is used also for etching of the oxide film on a semiconductor wafer.
[0003] Such a plasma [especially] characterized with a very low pressure, low ion energy (4-10eV), and high ion density is corrosive (corrosive).
[0004] Nowak which applied for the ceramic material on April 26, 1994 ** -- the U.S. patent application -- serial -- it is used in order to produce components, such as CVD reactor which was indicated by No.08 / No. 234,746 Typical (exemplary) CVD reactor is shown in drawing 1 . This typical reactor contains the vacuum chamber 10, the vacuum pump 12, and this insufflation nozzle 14 connected to the gas supply ring manifold 16 into the metal housing 18 which supports the insufflation nozzle (gas injection nozzles) 14. This chamber 10 has wall - or the sealing 20 which consists of a ring (annulus) 22 of the shape (hemispherical) of the shape (dome-shaped) of a partial dome surrounding the even disk (planar disk) 24, and a semi-sphere. The ring 22 of the shape of this dome consists of an insulator (insulator), and is supporting the RF (helically coiled) (RF) antenna 26 rolled spirally. Sealing 24 consists of a conductor. The base of a chamber 10 may contain the wafer pedestal 44 for holding a wafer 45, and may contain dielectric ring 44a which is on the same flat surface as the upper front face (top surface) of a wafer 45 (coplanar with), and surrounds a wafer 45 preferably. the wafer pedestal 44 -- a chuck, especially electrostatic -- you may include the characteristic feature or device (features) like a **** chuck
[0005] In the typical reactor of drawing 1 , the component containing the insufflation nozzle 14, the semi-sphere-like ring 22, the wafer pedestal 44, and dielectric ring 44a consists of a material of plasma fluorine resistance, such as a ceramic material, preferably. It is desirable that other components used in common in the process of a semiconductor, for example, a heater plate, a susceptor, a shield ring (ring), and a wafer boat (boat) also consist of such a material.
[0006] make most materials artificial (man-made) -- it was generated automatically -- an imitation -- the resistance over a plasma fluorine is inadequate and it is etched very quickly under a plasma fluorine

environment Most known materials which can bear a high-density fluorine plasma cannot be found (few). Theoretically, it was expected that high-grade alumina ceramicss, such as a sapphire or 99.9% alumina, showed endurance (prolonged resistance) to a low energy and a high-density fluorine plasma over a long period of time (for example, see the Lee et al. and J.Appl.Phys.68 (10) November 15, 1990 issue). Such a material forms an aluminum-fluoride (AlF) layer in case of exposure (exposure) to a fluorine plasma, and it is thought that it acts so that this may carry out the passivation of this material. Although having been tested is well-known as for the pure single crystal alumina slack sapphire, it is used under the high-density fluorine plasma environment where are one of the latest etching materials and it has a high-density fluorine plasma in the etch rate of about 50A / hour, and the temperature of 573-650K by the low energy (4-10eV) in inside.

[0007] However, as for the polycrystal alumina ceramics, being etched at the speed of 300-2000A is observed under the same condition. Typically, a polycrystal alumina ceramics consists of about 99.5 - 99.9% of an alumina, and binder phases, such as about 0.5 - 0.1% of a silica. A typical industrial polycrystal alumina ceramics shows the microstructure (microstructure) which has the congruence mode in the particle size (grain size) which is shown in drawing 2 or a distribution of ****** (bimodal), i.e., the distribution which has two values with the highest frequency over all the domains of particle size. Drawing 3 shows the typical congruence mode particle size distribution of the polycrystal alumina ceramic of such conventional technique.

[0008]

[Problem(s) to be Solved by the Invention] The microstructure in the congruence mode of the polycrystal alumina ceramics of the conventional technique gives the physical intensity which was excellent to this ceramics. However, typically, such an alumina ceramics will contain big "the field (silica-rich areas) which is rich in a silica" surrounding a parvus grain as a result of the particle size distribution in the congruence mode. Such "a field which is rich in a silica" can be easily seen all over drawing 2 . This "field which is rich in a silica" tends [very] to receive a fluorine attack, and, typically, it is etched the speed 96000A / more than hour in case of exposure to the high-density plasma fluorine of a low energy. If this silica binder is lost, the parvus grain of the alumina embedded at this will separate (the so-called "the grain drawing (grain pull-out)"), and will form the grain of the oxy-fluoride (oxyfluoride) of aluminum. Consequently, the well-known alumina ceramics has often collapsed typically, emitting the grain of an aluminum oxy-fluoride with a diameter of 0.1-2 micrometers into CVD chamber.

[0009] It will be desirable to offer the polycrystal alumina ceramic material which shows the resistance improved to the plasma fluorine. Such a material will be easy for finding out the application in a production of the component in vacuum process equipments, such as CVD or an etching chamber. It will be still desirable to offer technique to have been improved for producing this new ceramic material.

[0010]

[Means for Solving the Problem] If the one side face (aspect) of this invention is followed, the polycrystal alumina ceramic material of plasma fluorine resistance will be offered.

[0011] If the specific side face is followed from this invention's, this ceramic material contains about 99.5 - 99.8% of an alumina, and about 0.5 - 0.2% of a binder by the weight.

[0012] If other specific side faces of this invention are followed, this alumina ceramic material has the single mode or the particle size distribution of single **** (unimodal), and a distribution (centered) especially centering on about 15 micrometers - 30 micrometers.

[0013] If other side faces of this invention are followed, the technique for producing the polycrystal alumina ceramic material of plasma fluorine resistance includes the process which forms the base or plastic matter (green body) which has the particle size distribution in the single mode, and the process which sinters this base, including about 99.5 - 99.8% of the weight of an alumina, and about 0.5 - 0.2% of the weight of a binder.

[0014] If the side face of further others of this invention is followed, the product which the ceramic material produced according to the above-mentioned technique is offered, and consists of this ceramic material will be offered.

[0015] Other purposes, characteristic features, and advantages of this invention will become clear from the following detailed explanations for this contractor. However, these detailed explanations and specific examples accompanied by the suitable mode of this invention being shown are instantiation, and if not restrictive, he should understand them. Many change or corrections are possible, without separating from the pneuma within the limits of this invention, and this invention includes all of such corrections.
[0016] By referring to an attached drawing, this invention will be understood more easily.
[0017]
[Embodiments of the Invention] The polycrystal alumina ceramic material into which we have a single mode distribution of particle size discovered that it was very resistance to the attack of a plasma fluorine.
[0018] 1. The material of property this invention of the material (inventive) of invention contains an about 99.5 wts% - about 99.8 wts% alumina. A silica and the mixture of CaO and MgO are included in a binder and a type target remaining about 0.5 wts% - 0.2wt%. It is useful that MgO is included in order to help grain growth control in this binder.
[0019] This material is characterized by distribution in the single mode of alumina particle size. The vocabulary with the "single mode" says that the (on the contrary [the value which is two with the highest frequency of distributions in the congruence mode]) distribution has the value of a single particle size with the highest frequency, i.e., the mode.
[0020] The distribution has more preferably about 15 micrometers - 30 micrometers of centers in between [about 20 to 25] (centered). That is, the mode of this distribution enters between the domains of the value mentioned above. This distribution contains still preferably less than 10% which has the size of less than about 10 micrometers of a grain, and less than [which has a size exceeding about 30 micrometers / of a grain] 10.
[0021] the distribution in the single mode which has a center in parvus particle size (especially 8 micrometers - less than 12 micrometers) farther than about 15 micrometers gives the ceramic material which shows unsuitable resistance to a plasma fluorine (the amount of a lot of [especially] binders than about 0.5 wts% -- although -- the time of being used) The distribution in the single mode which has a center in a large particle size more nearly intentionally (significantly) than 25 micrometers may give the ceramic material which has an unsuitable intensity (intensity which is in inverse proportion to the square root of particle size).
[0022] Drawing 4 shows the typical polycrystal alumina ceramic material of this invention. There is "few fields which is rich in a silica" surrounding the parvus grain to which the material of invention illustrated as compared with the material shown in drawing 2 was isolated far. The distribution in the single mode of the particle-size property of the material illustrated invention is shown all over drawing 5 .
[0023] The material of invention is characterized by the outstanding resistance over a fluorine plasma. The average weight (gravimetric) etch rate of about 150A / hour calculated based on 20 hour exposure to a plasma fluorine is attained easily. Converging a weight etch rate on the etch rate, or 50A / hour of a sapphire about is observed for a long period of time which is measured after exposure of 35 hours to a plasma fluorine (see the drawing 6).
[0024] As shown all over drawing 6 , the observed weight etch rate is nonlinear to time. The ceramic material (black dot) of invention is quite quick at the beginning, and it is etched. This is reflecting elimination of the surface silica phase generated between baking (firing) of the material of invention. After removing a surface silica phase, an apparent (apparent) etch rate decreases. In this organization (regime), this plasma etches a silica binder phase along with a grain boundary (grain boundaries). As shown in the drawings 7 , 8, and 9 showing a grain-boundary aspect ratio after exposing the sample which consists of a 99.5% alumina ceramic material of this invention to a plasma fluorine for 0 hour, 5 hours, and 35 hours, the aspect ratio (height to width of face) of the grain boundary increases, as etching advances. Once this aspect ratio exceeds the about 5 average, there is nothing for which a grain boundary is permeated effectively any longer so that it may continue that the plasma etches a silica binder (penetrates). Therefore, in a long exposure, an etch rate approaches it (black trigonum) of a

sapphire.

[0025] Also in the reduced weight etch rate, a comparative high purity alumina (black dot) shows etching behavior (behavior) similar in all organization. The reduced etch rate is considered [which exists in this material] to be more based on a parvus silica volume. However, in spite of acquiring the improved weight etching resistance, this high purity alumina is troubled with higher "grain drawing" compared with the alumina of invention so that it may be proved by the comparison with drawings 10 and 11. This higher "grain drawing" can be similarly returned to the lowness of the existing silica volume. It is thought that a high-grade material separates grain more easily compared with the material which does not have sufficient volume of the binder for developing suitable grain indirect arrival (intra-granular adhesion), therefore has lower purity, i.e., a larger binder volume.

[0026] The thing with the very low (< 100A /, hour) etch rate to each alumina grain in the ceramic material of invention is found out.

[0027] The polycrystal alumina ceramic material of this invention has the very desirable physical property which includes an intensity and a high density, or high thermal shock resistance. Typical compressive strength (compressive strength) is at least 300 and 000psi. Flexural strength (flexual strength) is at least 40 and 000psi typically. the density after sintering -- typical -- at least -- about 3.75 -- g/cm3 it is . Thermal shock (thermal shock) **T is about 200 degrees C typically.

[0028] 2. The technique for producing the polycrystal alumina ceramic material of production invention of the material of invention includes a control of the baking sequence (firing sequence) used during sintering of this base for producing a control of the distribution of the beginning of particle size in the fine-particles raw material (powdered material) used in order to form the first base (green body), and a desired final product.

[0029] the beginning -- about 99.5 -- a wt%-99.8wt% alumina -- the -- a residue (balance) -- the fine particles which have the particle size distribution in the single mode are produced, including the selected binder Such a distribution can be obtained by sieving (sieving) for obtaining a distribution of trituration (milling) processes, such as for example, ball mill trituration, and the request which follows this (followed by). other trituration processes, the thing which a sieving step follows preferably, and ** -- it is usable The particle size distribution in the original single mode has a center in about 0.5 micrometers - about 2.0 micrometers preferably.

[0030] Once, if the particle size distribution in the desired single mode is generated, these alumina fine particles will be formed in a base (namely, the original non-sintered compact which consists of the miniaturized fine particles). In formation of this base, it is desirable to control the dimension (dimensions) of this material so that homogeneity of the temperature between sintering is realized.

[0031] Especially the thing for which this base is formed in desired final type is useful so that additional machining may not be required after sintering. "Calcinating" (as-fired) goods show the resistance improved [as opposed to / the plasma fluorine / especially] so that a detail may inquire more below. / which is produced as a result

[0032] The pressure used in order to produce a base is the domain of about 5000 to 14000 psia (preferably about 7000-10 and 000psia) preferably. The original base density is 3 about 1.8-2.2g/cm preferably. It is a domain.

[0033] Once this base is formed, it will be set to a distribution in the single mode of a desired final particle size, and sufficient sufficient time and temperature to attain for about 15 micrometers - 30 micrometers preferably. And it is sufficient density to attain a permissible intensity (preferably at least 3.75g/cm 3, typically about 3.8g/cm 3). Non-pressure (pressureless) sintering (namely, sintering by the environmental pressure (ambient presure)) is presented. The minimum compressive strength is about 300 and 000 psi preferably. The minimum flexural strength is about 40 and 000 psi preferably.

[0034] Preferably, about 1400-1700 degrees C, a non-pressure sintering process is about 1600-1650 degrees C in temperature, is the time of 7 - 8 hours preferably, and is performed in air (air) for 1 to 10 hours.

[0035] Preferably, in case the process of invention forms various products and the product used in the environment where plasma fluorine exposure is presented with them, it gives the alumina ceramic

material of usable plasma fluorine resistance. Such a product includes a bell jar (bell jars), a crucible, and the component used with vacuum process equipment. The more concrete product which enters within the limits of this invention includes the component of the vacuum process equipment like a chuck, a nozzle, a susceptor, a heater plate, a clamp ring, a shield ring, a wafer boat, or a chamber wall. What is necessary is just to have the layer containing the ceramic material of this invention into one, or the front face or fraction beyond it that such a product should just consist of a ceramic material of this invention on the whole or substantially.

[0036] The mean etch rate of a ceramic material which has the front face which should be surprised, and where "a manipulation after baking" manipulation of polishing, a lapping, etc. Making is also especially exposed to a plasma fluorine shows larger resistance to a fluorine attack. It is etched at the parvus and the speed of a maximum of 20% from the same material (otherwise identical materials) by other technique that the material ["being calcinated"] was processed after baking. [such] According to these materials, the etch rate of about 130A / hour (based on exposure for 20 hours) is realized easily. [under]

[0037] this invention is explained further, referring to the following un-restricting-examples.

[0038]

[Example]

The polycrystal alumina ceramic material which has the particle size distribution in the example 1 single mode was produced as follows. Alumina fine particles were produced by mill trituration (milling) of 6 hours in the inside of a ball mill. these fine particles are applied to a sieving, give the fine particles which have the particle size distribution in the single mode centering on 2 micrometers, and combine them with a fine-particles-like silica (powdered silica) -- having -- a 99.5wt% alumina, a 0.3wt% silica, and the remainders MgO and CaO -- since -- the becoming constituent was given

[0039] It has a dimension with a diameter [of 2.5cm], and a thickness of 1.0cm, and this constituent is 3 2.2g/cm under the pressure of 8000psias. It was formed in the base of having a density. 1600 degrees C of non-pressure sintering of this base were performed in air for 8 hours. The polycrystal alumina ceramic material produced as a result is 3 3.8g/cm. It had the density and the particle size distribution in the single mode centering on 20 micrometers.

[0040] the material of invention is machined after baking (polishing) -- having (machined) -- or CF4 which is maintained in the state of ** "calcinated", and subsequently has the following parameters : O2 It was exposed to the plasma.

[0041]

Composition CF4 : O2 and 10 : Flow rate of 1 (flow ratio)

Pressure 30mTorr coupon (Coupon) temperature 300 degree-C plasma potential 10V RF (RF) power 2500W plasma density 5x1011 ion / cm3RGA ion analysis CF3, CF2, and CF, F, O (order in which concentration is decreasing)

As for the material of invention, 20 hours was exposed.

[0042] The comparison coupon consisted of the well-known alumina, an aluminium nitride and a ceramic material, and a sapphire, and was exposed to the plasma by the same technique.

[0043] The weight etch rate was calculated about each material based on measurement and a true-density (true density) calculation of the decrease of a weight based on exposure of 20 hours. A result is as follows. (The maximum error, **15A / hour) .

[0044]

[Table 1]

セラミック	エッチング速度（オングストローム/hour）	
	研磨	焼成のまま
WesgoA１－９９５ ９９．５％アルミナ	４３８	３２０
KyoceraA４７９ ９９．５％アルミナ	４４０	…
KyoceraA４８０ ９９．９５％アルミナ	８３０	…
KyoceraSA－１００ 単結晶サファイヤ	７０	７０
NGKAN－１１ ９９．９％窒化アルミニウム	１５３	…
発明品	１５２	１２７

[0045] The polycrystal alumina ceramic material of invention shows the resistance which was excellent to the plasma fluorine compared with a well-known polycrystal alumina, and is excellent in the comparison with an aluminium nitride and a sapphire so that clearly from the above-mentioned table.
[0046]
[Effect of the Invention] About a "grain drawing", the material of invention conquers the distress accompanied by the alumina ceramic material of the conventional technique, and its production is simple and it serves as the medium (medium) for cheap mass production method of the component of a vacuum evaporation system, and other products.

[Translation done.]

* NOTICES *

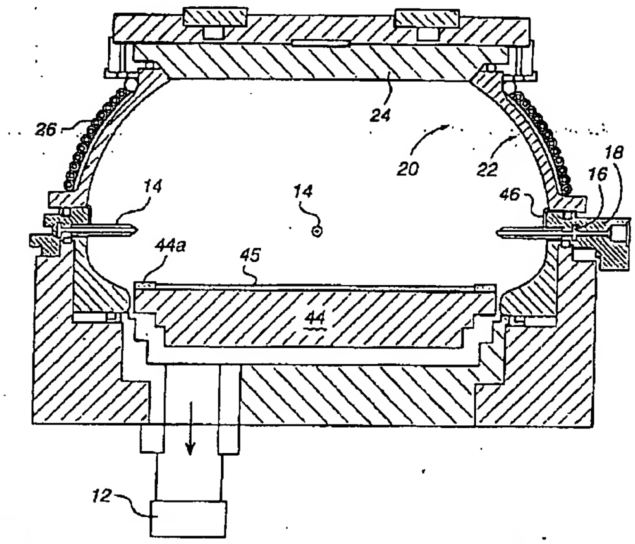
DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the cross section of typical CVD reactor. These various components consist of a polycrystal alumina ceramic material of this invention preferably.
[Drawing 2] It is the light microscope photograph (one 266 times the scale factor of this) of the polycrystal alumina ceramic material of the conventional technique, and the congruence mode particle size distribution of 6.8 micrometers of mean particle diameters is shown.
[Drawing 3] They are a particle-size-number of the polycrystal alumina ceramic material of the conventional technique of graphs which have a congruence mode distribution of particle size.
[Drawing 4] It is the light microscope photograph (one 266 times the scale factor of this) of the polycrystal alumina ceramic material of this invention, and the single mode particle size distribution of 20 micrometers of mean particle diameters is shown.
[Drawing 5] They are a particle-size-number of a polycrystal alumina ceramic material of graphs shown in view (inventive) 3 of invention which has a single mode distribution of particle size.
[Drawing 6] CF4 of the 99.5wt% alumina ceramic material (black rectangular head) in which an exposure front face has the silica binder of this invention ground before this exposure (ground), a high-grade (99.9wt%) polycrystal alumina (black dot), and a sapphire (black trigonum) : O 2 = 10: It is the graph of the etch-rate-time at the time of using ICP plasma (30mTorr, 2500W) of 1. The long convergence (long-term convergence) to an etch rate is shown to the sapphire of the etch rate of the material of invention.
[Drawing 7] It is drawing showing the grain-boundary aspect ratio at the time of exposing 99.5% alumina ceramic material of this invention to a plasma fluorine for 0 hour (grain boundary aspect ratio).
[Drawing 8] It is drawing showing the grain-boundary aspect ratio at the time of exposing 99.5% alumina ceramic material of this invention to a plasma fluorine for 5 hours.
[Drawing 9] It is drawing showing the grain-boundary aspect ratio at the time of exposing 99.5% alumina ceramic material of this invention to a plasma fluorine for 35 hours.
[Drawing 10] It is the comparative scanning-electron-microscope (SEM) photograph (one 4000 times the scale factor of this) of a high-grade 99.9wt% polycrystal alumina ceramic material before exposure to a plasma fluorine.
[Drawing 11] It is the comparative scanning-electron-microscope (SEM) photograph (one 4000 times the scale factor of this) of a high-grade 99.9wt% polycrystal alumina ceramic material after 35 hour exposure to a plasma fluorine. The surface damage to the material of the conventional technique produced by exposure to this plasma is shown.

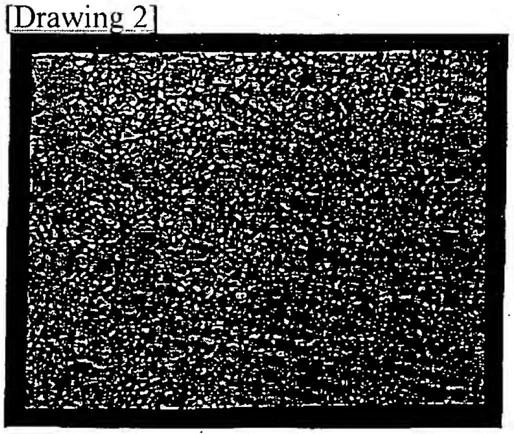
[Translation done.]

DRAWINGS

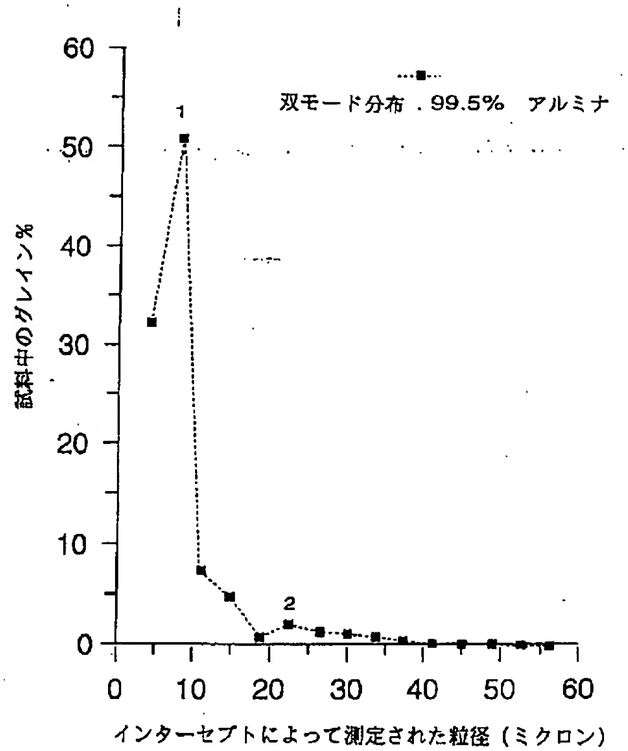
[Drawing 1]



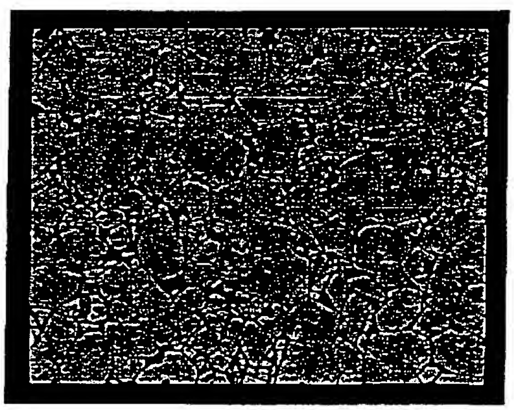
[Drawing 2]



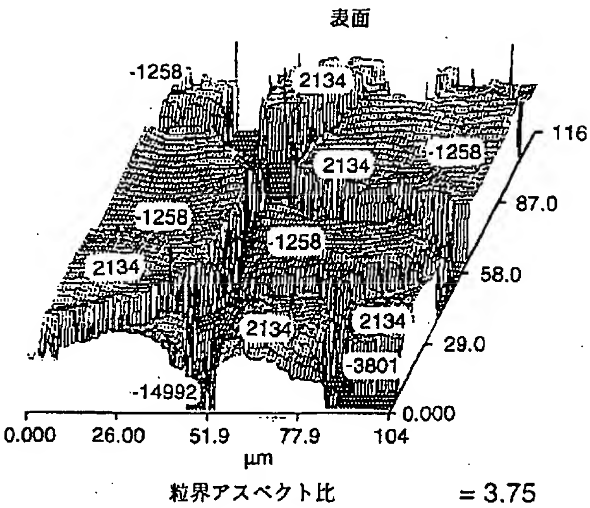
[Drawing 3]



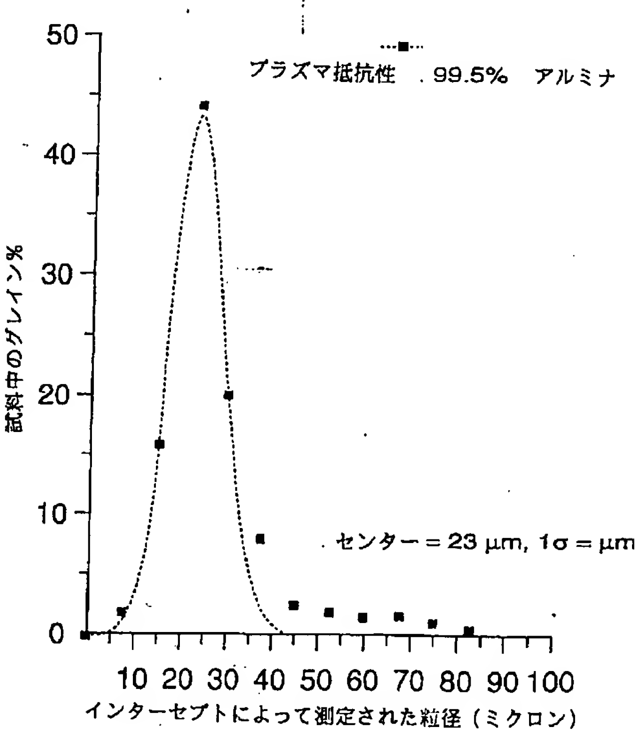
[Drawing 4]



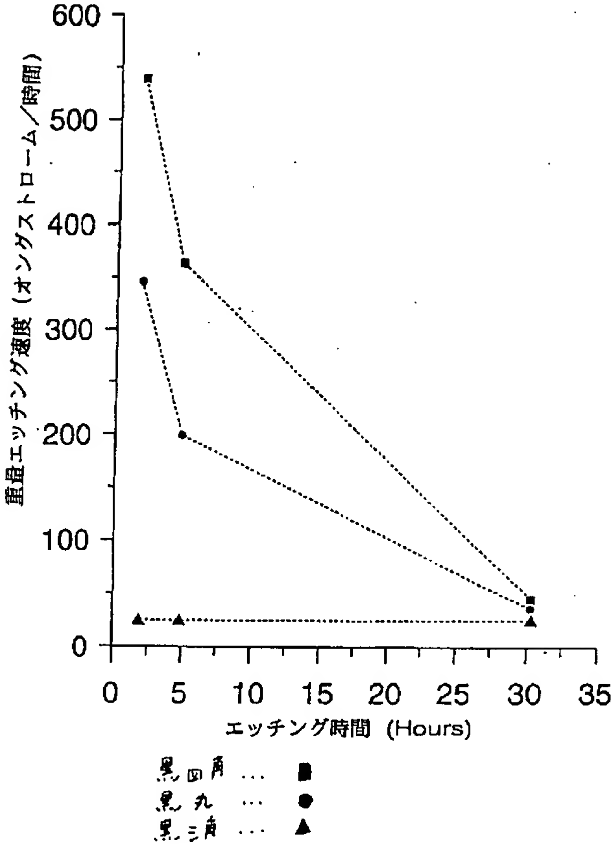
[Drawing 7]



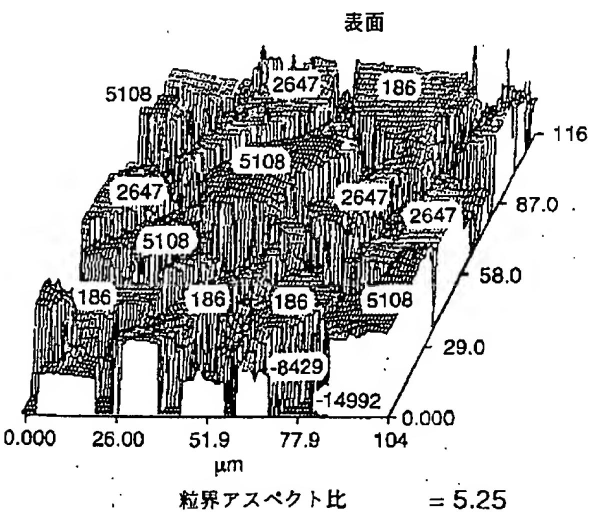
[Drawing 5]



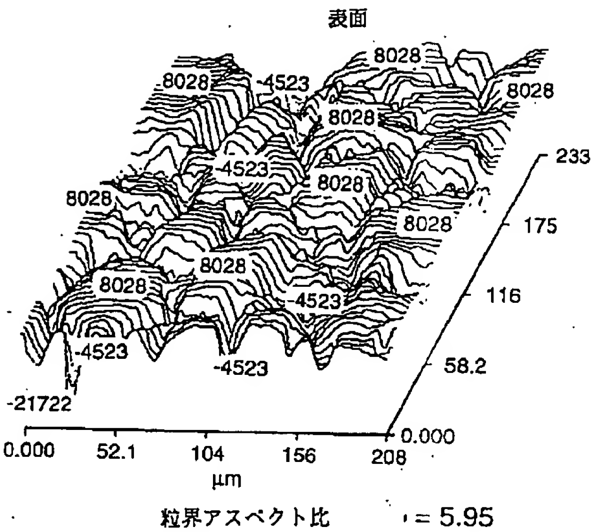
[Drawing 6]



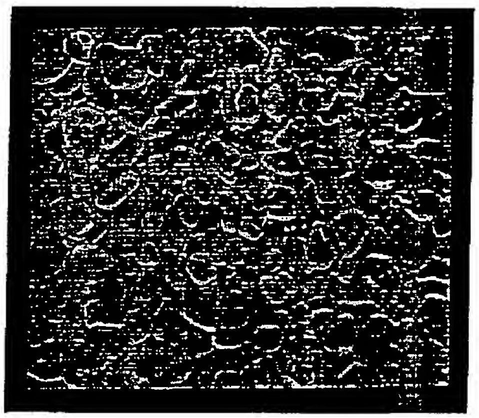
[Drawing 8]



[Drawing 9]

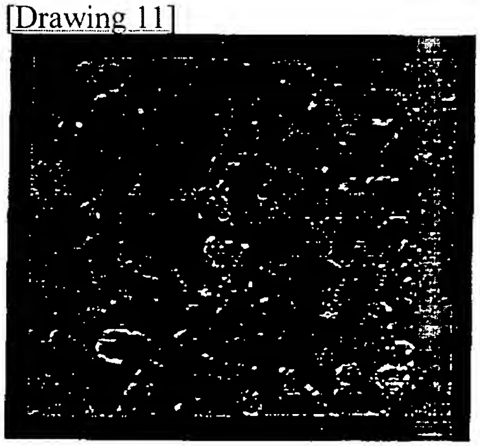


[Drawing 10]



(先行技術)

[Drawing 11]



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[Translation done.]